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Modification of the Activity of Chromia and Chromia-Alumina Catalysts by Adsorbates

J. C. KURIACOSE, C. DANIEL, AND R. SWAMINATHAN

From the Department of Chemistry, Indian Institute of Technology, Madras 36, India

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The parallel dehydrogenation and dehydration of cyclohexanol and isopropanol on chromia show that the selectivity is determined, not by the catalyst alone, but by both, the absorbate and the catalyst. The dehydrogenation of the alcohols on chromia and chromia-alumina is enhanced when they are mixed with acetic acid or hydrogen. Cyclohexane suppresses the dehydrogenation. These observations are discussed in the light of the effect the chemisorption of the various compounds has on the electronic character of the catalyst. It is seen that the effect of doping semiconductor oxides can be simulated by mixing reactants with other substances.

INTRODUCTION

A survey of the literature reveals that the catalytic properties of solid catalysts can be selectively controlled by introducing appropriate foreign ions in the catalyst. The electronic changes taking place in a catalyst during a dehydrogenation reaction and the changes in the electronic properties and activity of the catalyst caused by the introduction of foreign ions into it have been studied by many workers (*1–3*). It was considered interesting to investigate whether the chemisorption of a gas or vapor could be used to alter the activity of the catalyst in a controlled manner. Doping chromia catalysts with altervalent ions to effect a change in the electronic properties, and hence the catalytic activity, has been tried by Upreti *et al.* (*4*). The work reported here, suggests the possibility of controlling the activity of chromia catalysts by mixing the reactant, an alcohol, with another gas or vapor to obtain effects similar to doping.

METHODS

A flow-type reactor held in a slightly inclined position in a furnace, the temperature of which could be controlled with an energy regulator, was employed for these studies. The slight inclination of the furnace, while permitting easy flow of reactants and products, minimized the chances of temperature gradients in the reactor arising from a vertical mounting. The reactant was fed by controlled displacement of the liquid with mercury. The chromia-alumina catalyst was kindly supplied by the Houdry Process Corporation. The chromia catalyst was prepared by precipitating the hydroxide from chromium nitrate with ammonia according to the procedure suggested by Pandao *et al.* (*5*). The catalyst was conditioned by treatment with carbon dioxide-free dry air at 500°C for 6 hr and pure dry hydrogen at the same temperature for 8 hr. After every experiment, the catalyst was regenerated by passing dry air for 4 hr followed by dry hydrogen for 6 hr over the catalyst at 500°C. The catalyst activity and selectivity given by the ratio of dehydrogenation to dehydration were determined by conducting check runs after each set of experiments, to ensure their constancy.

The liquid products were all analyzed by vapor-phase chromatography using either a Carbowax column or a Hallcomid column at 70°C. The gaseous products were analyzed using an Orsat apparatus and also by vapor-phase chromatography with a dimethylsulfolane column at room temperature.

The thermoelectric potentials of the catalysts at temperatures above 400°C were measured by placing the catalyst in a Pyrex glass boat provided with two sealed-in platinum wires which served as electrical contacts to measure the thermovoltage. One of the terminals was in the form of a loop and so the two ends of the loop were connected to a rectifier from which a desired potential could be applied to heat the part of the catalyst with which the loop was in contact. Measurements were made using zinc oxide also under identical conditions and a comparison of the direction of the thermovoltage measured with a nanoamperometer made. The change in the resistance of the catalyst in different atmospheres was measured with the aid of a vacuum tube voltmeter.

RESULTS

Cyclohexanol and isopropanol undergo both dehydrogenation and dehydration on chromia and chromia-alumina catalysts. The former gives cyclohexanone and cyclohexene and the latter acetone and propylene. At 460°C and low contact time of the order of 0.1 sec, the selectivity given by the ratio of dehydration to dehydrogenation is in favor of dehydration for cyclohexanol (1.4) and dehydrogenation for isopropanol (0.28) on a chromia catalyst. Using helium as well as nitrogen as diluents it was found that the selectivity does not depend on the partial pressure of the alcohol.

Acetic acid reacts to give acetone, carbon dioxide, and water. In order to obtain information about the nature of the catalytic activity that leads to ketonization, mixtures of acetic acid and isopropanol or cyclohexanol were studied. When these mixtures were reacted over chromia at 460°C at a contact time of 0.7 sec, it was observed that the ketonization is inhibited to a considerable

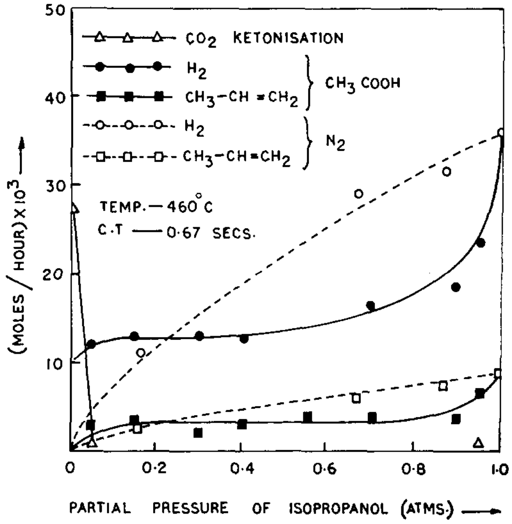

FIG. 2. Effect of nitrogen and acetic acid on the reaction of isopropanol.

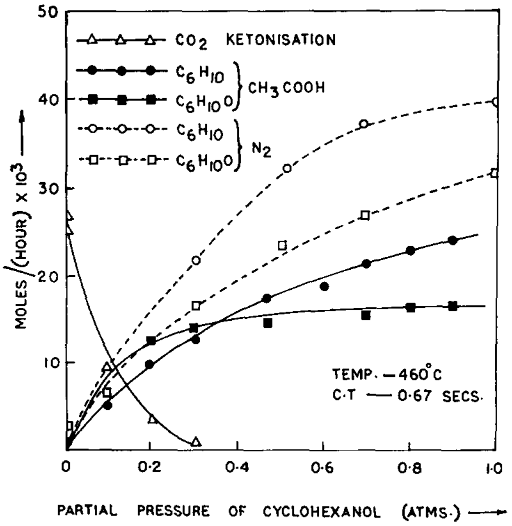

FIG. 1. Effect of nitrogen and acetic acid on the reaction of cyclohexanol.

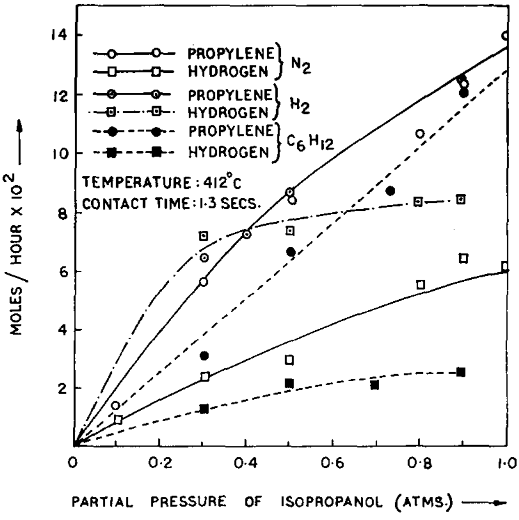

FIG. 3. Effect of nitrogen, hydrogen, and cyclohexane on the reaction of isopropanol.

TABLE 1
PERCENTAGE CONVERSION OF ISOPROPANOL ON CHROMIA AT VARIOUS PARTIAL PRESSURES WHEN DILUTED WITH NITROGEN AND ACETIC ACID[a]

Partial pressure of alcohol (atm)	Diluent: acetic acid			Diluent: nitrogen		
	H_2	H_2O	Total conversion	H_2	H_2O	Total conversion
1.0	20.2	4.3	24.5	20.2	4.3	24.5
0.78	9.6	1.9	11.5	24.8	5.2	30.0
0.69	9.5	2.1	11.6	25.8	5.3	31.1
0.36	15.8	3.6	19.4	20.2	5.6	25.8
0.11	48.7	10.2	58.9	19.1	3.7	22.8

[a] Temperature, 460°C; contact time, 0.67 sec; wt of catalyst, 1.5 g.

extent. The dehydration of the two alcohols is suppressed by acetic acid at all partial pressures. At very high partial pressures of acid, there is an enhancement of the dehydrogenation of the alcohols, but as the partial pressure of acid decreases, there is inhibition. The enhancement of dehydrogenation is more pronounced in the case of isopropanol than in the case of cyclohexanol. At low partial pressures of acid, the relative inhibition is greater for dehydration in the case of cyclohexanol, and dehydrogenation in the case of isopropanol, as can be seen from Figs. 1 and 2. There is no indication of any esterification.

A comparison of the results for the reaction of isopropanol in mixture with hydrogen or cyclohexane, with those obtained when isopropanol is diluted with nitrogen, indicates that hydrogen enhances the dehydrogenation while cyclohexane suppresses it (Fig. 3). At 412°C on chromia-alumina there was little dehydrogenation of cyclohexane. The influence on dehydration is not so marked. Cyclohexane was chosen as a substance to be mixed with isopropanol because on adsorption on the catalysts it modifies the electrical resistance of the catalyst in a manner similar to hydrogen. The percentages of isopropanol actually reacted at the various partial pressures when mixed with acetic acid, hydrogen, and cyclo-

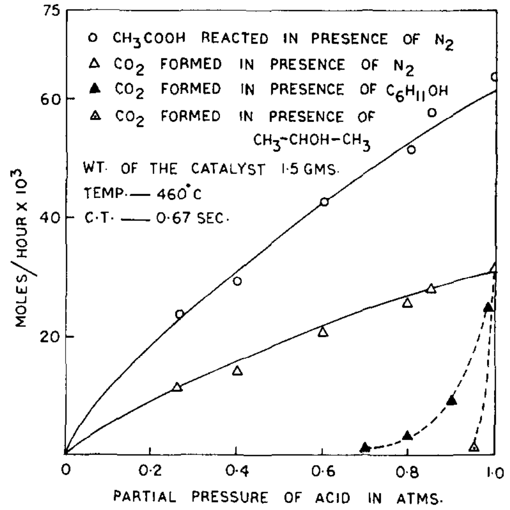

FIG. 4. Effect of nitrogen, cyclohexanol, and isopropyl alcohol on the reaction of acetic acid.

TABLE 2
PERCENTAGE CONVERSION OF CYCLOHEXANOL ON CHROMIA AT VARIOUS PARTIAL PRESSURES WHEN DILUTED WITH NITROGEN AND ACETIC ACID[a]

Partial pressure of alcohol (atm)	Diluent: acetic acid			Diluent: nitrogen		
	H_2	H_2O	Total conversion	H_2	H_2O	Total conversion
1.0	13.5	17.2	30.7	13.5	17.2	30.7
0.69	10.0	13.8	23.8	16.9	22.8	39.7
0.50	13.0	15.2	28.2	20.2	27.3	47.5
0.30	19.9	18.5	38.4	23.8	31.1	54.9
0.10	14.3	8.0	22.3	12.5	17.0	29.5

[a] Temperature, 460°C; contact time, 0.67 sec; wt of catalyst, 1.5 g.

TABLE 3

Percentage Conversion of Isopropanol on Chromia-Alumina at Various Partial Pressures When Diluted with Nitrogen, Hydrogen, and Cyclohexane[a]

Partial pressure of alcohol (atm)	Diluent: nitrogen		Diluent: hydrogen		Diluent: cyclohexane	
	H_2	H_2O	H_2	H_2O	H_2	H_2O
1.0	11.8	22.2	11.8	22.2	11.8	22.2
0.9	12.0	22.5	15.9	23.1	4.9	17.1
0.8	12.3	22.6	17.7	23.2	—	—
0.5	12.6	28.8	20.6	29.2	7.2	22.2
0.3	13.6	31.9	28.6	32.8	7.3	24.5
0.1	16.6	33.3	—	—	—	—

[a] Temperature, 412°C; contact time, 1.3 sec; wt of catalyst, 4.5 g.

hexane are presented in Tables 1, 2, and 3. The behavior of acetic acid when diluted with nitrogen is shown in Fig. 4. The effect of cyclohexanol and isopropanol on the ketonization reaction is also represented in the same figure. It will be noted that relatively low partial pressures of alcohols completely suppress the ketonization reaction.

A comparison of the thermoelectric potential of chromia and chromia-alumina with that of zinc oxide indicates that at temperatures above 400°C, they behave like *n*-type semiconductors. Chemisorption of acetic acid above 400°C leads to an increase in the conductance while chemisorption of hydrogen, cyclohexane, and isopropanol diminishes the conductance.

Discussion

The fact that chromia favors dehydration of cyclohexanol and dehydrogenation of isopropanol shows that the dehydration and dehydrogenation activities of the catalyst are not functions of the catalyst alone. The interaction between the adsorbate and the catalyst is at least as important as the intrinsic nature of the catalyst in determining the degree of activity.

The enhancement of the dehydrogenation of isopropanol when mixed with hydrogen can be attributed to two causes. When the conversion is high, the presence of hydrogen may keep the surface clean by preventing the large amounts of products formed from undergoing side reactions which might lead to polymerization and coke formation. Thus the activity of the catalyst may be maintained at its initial level by the added hydrogen whereas if the hydrogen were not present the activity would have fallen. The other possibility is that hydrogen modifies the nature of the surface, increasing its activity.

The analysis of the gases formed during the heating in oxygen of a catalyst sample used for the dehydrogenation of pure isopropanol showed little evidence for the presence of carbon dioxide. The material balance worked out at the end of a dehydrogenation experiment with pure isopropanol indicated no loss of material. Further, the vapor-phase chromatographic analysis of the liquid and gaseous products did not reveal any products other than acetone, water, propylene, and hydrogen. It is therefore unlikely that hydrogen enhances the dehydrogenation activity of the catalyst by just helping to keep the surface clean by preventing polymerization and coke formation.

Adsorption of hydrogen on chromia and chromia-alumina above 400°C decreases the conductance of the catalyst and hence must involve the trapping of the current carriers. Under the same conditions alcohol adsorption also produces the same electrical effect. Hence, one would expect that if a mixture of hydrogen and isopropanol is used, the hydrogen would suppress the adsorption of alcohol and reduce the rate of dehydrogenation. The opposite effect is observed, suggesting that the adsorption of hydrogen conditions the surface to make it more active for dehydrogenation. Since the current carriers are electrons, this implies that isopropanol will dehydrogenate along a less energetic path on a relatively electron-deficient surface. This is in agreement with Hauffe's observation (*1*) that lithium doping of zinc oxide leads to enhanced activity for dehydrogenation of isopropanol.

The ketonization of acetic acid on basic oxides has been considered to take place through the intermediate formation of salts. As can be seen from Fig. 4, the ketonization on chromia is considerably suppressed by isopropanol and cyclohexanol, even though acetic acid in turn suppresses their dehydration and dehydrogenation. The mechanism of this ketonization of acetic acid is presently under study and the data obtained so far suggest the interaction of two adsorbed acetic acid molecules through probably an acetate ion and an acyl carbonium ion to form acetone.

The inhibition of both dehydrogenation and dehydration by very low partial pressures of acetic acid shows that it covers part of the catalyst surface at all partial pressures, making the surface unavailable for isopropanol. In spite of this reduction of available surface by the acetic acid, at high partial pressures acetic acid enhances the dehydrogenation. The electrical conductivity measurements on the catalyst reveal that the adsorbed acetic acid increases the conductivity of the catalyst, which means that it makes electrons available to the catalyst. Since isopropanol on adsorption accepts electrons from the catalyst, acetic acid adsorption can help an enhanced adsorption of isopropanol. Enhancement of the adsorption of one adsorbate by another adsorbate has been observed in cases such as mixtures of carbon monoxide and hydrogen on methanol synthesis catalysts (*6*, *7*). At low partial pressures of isopropanol the enhancement in dehydrogenation observed may be due to the amount of isopropanol adsorbed in the presence of acetic acid being more that than in the presence of nitrogen. However, as the partial pressure of alcohol approaches the saturation value, the diminution in available surface due to the strong adsorption of acetic acid may not be compensated for by the beneficial effect introduced in the nature of the surface by the acetic acid. An alternate explanation would be that the presence of large proportions of acetic acid makes the properties of the vapor phase more conducive to the alcohol being adsorbed in a manner favorable for dehydrogenation. This could be similar to solvent effects observed in solution reactions.

The conductivity data for the catalysts in the presence of cyclohexane do not support Hauffe's suggestion (*1*) that cyclohexane loses an electron to the surface on adsorption. Cyclohexane, which appears to undergo a similar electronic interaction with the surface as hydrogen, actually suppresses the dehydrogenation without itself undergoing any reaction. The cyclohexane structure may not permit a sufficiently strong interaction with the surface to cause the separation and abstraction of hydrogen from itself. The suppression of dehydrogenation of isopropanol caused by the cyclohexane in spite of its inducement of electronic effects similar to that caused by hydrogen, may be due to the size of the cyclohexane molecule which, mole for mole, occupies much more surface than hydrogen. The cyclohexane, like hydrogen, may be making it possible for the isopropanol to dehydrogenate along a less energetic path, but the surface concentration of isopropanol may not be sufficient to make the overall rate of dehydrogenation greater than that in the presence of nitrogen as diluent. The beneficent electronic effect may not be of sufficient magnitude to compensate for the decrease in available surface area.

Whenever there is suppression of activity, it might be possible to attribute it to the usual covering up of the surface, thus making it unavailable for the reactants. But enhancement of the activity cannot be attributed to such a cause. Hydrogen could not be altering the characteristics of the vapor phase, as was suggested as a possibility in the case of acetic acid, to make it easier for the isopropanol to interact with the surface in a manner leading to dehydrogenation. Commensurate with the large enhancement in dehydrogenation that hydrogen brings about, one would expect that there would be enough coke formation or polymerization during the dehydrogenation of pure isopropanol to produce detectable amounts of carbon dioxide when the catalyst is heated in air as a part of the regeneration procedure. The absence of carbon dioxide permits one therefore to conclude that the augmentation of dehydrogenation observed in the case of all partial pressures of hydrogen, as well as higher partial pressures of acetic acid, is due to modification of the electronic properties of the catalyst surface caused by the adsorption of these substances.

CONCLUSION

The study of simultaneous reactions on chromia and chromia-alumina shows that the selectivity of the catalyst is not determined by the catalyst alone, but by the substrate also. The observed activity of the catalysts is a consequence of the kind of interaction that takes place between the catalyst and the substrate.

An enhancement in the activity for a particular reaction can be brought about by mixing the reactant with a suitable gas or vapor. It is suggested that this enhancement results from the added constituent aiding the reactant molecule to get adsorbed in the manner that provides the easiest path to reaction. The adsorption of the added constituent on the catalyst surface may also reduce the surface area available to the reactant. Often, both effects may operate and the net result may be a suppression of the activity because the beneficent modification of the surface may not compensate for the diminished surface available for the reactant.

The alteration in the activity caused by mixing reactants with other substances lasts only during the reaction and so does not permanently alter the activity of the catalyst. The results obtained indicate that what could be achieved by doping the catalyst can also be achieved by mixing other constituents with the reactant vapor. There is the added advantage that the nature of the catalyst suffers no permanent change.

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